

# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN AND RELATING TO PROCESSES FOR THE PRODUCTION OF REDUCING GAS

(71) We, NIPPON KOKAN KABUSHIKI KAISHA, a Japanese Body Corporate of 1-3, 1 chome, Ote-machi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to processes for the production of reducing gas.

According to this invention there is provided a process for the production of reducing gas which comprises feeding a mixture of preheated methane or a methane-containing gas at a temperature below 1100°C and a gas comprising CO<sub>2</sub> and/or H<sub>2</sub>O at a temperature above 1250°C into a reforming zone, and heating the mixture at a temperature of at least 1200°C whereby the mixture is reformed.

For a fuller understanding of the present invention, reference is made to the accompanying drawings wherein:—

25 Figure 1 is a graph showing the decomposition of methane with temperature;

Figure 2 is a graph showing the reaction between free carbon and CO<sub>2</sub> with time at various temperatures;

30 Figure 3 is a flow diagram;

Figure 4 is a modified form of the flow diagram of Figure 3; and

35 Figure 5 is a graph showing reaction of free carbon with CO<sub>2</sub> as a function of CO<sub>2</sub> concentration.

On heating the mixture of gases in a reforming zone at a temperature of at least 1200°C, methane present in the mixture is believed to decompose according to the following reactions:—



45 The reaction given in equation 1 is herein after called the methane decomposition reaction. Referring to Figure 1 of the accompanying drawings, the reaction does not occur

at temperatures below 900°C. However, it becomes pronounced at temperatures from 1000° to 1200°C and methane then undergoes 100% decomposition to form H<sub>2</sub> and active free carbon. The resulting free carbon is converted into CO by reaction with CO<sub>2</sub> according to the following equation:—



As can be seen from Figure 2, the amount of reaction increases as the reaction temperature and the reaction time are increased. However, a minimum temperature of about 1200°C is required. As described above, in order to form free carbon in the methane decomposition reaction and to cause the free carbon to react with H<sub>2</sub>O and/or CO<sub>2</sub> in the raw material gas for forming CO and H<sub>2</sub> which are required for reduction, the methane should generally be heated quickly.

A suitable source of the gas containing CO<sub>2</sub> and/or H<sub>2</sub>O includes, for example, the exhaust gas from a blast furnace. The methane-containing gas may, for example, be methane in admixture with nitrogen or coke oven gas. When methane is used in admixture with nitrogen, the mixture is preferably mixed with the gas containing CO<sub>2</sub> and/or H<sub>2</sub>O in a volume ratio of about 1:6. When coke oven gas is used as the methane-containing gas, the volume ratio of the methane-containing gas to the gas containing CO<sub>2</sub> and/or H<sub>2</sub>O is preferably about 1:2.

In a preferred embodiment of the present invention, and referring to Figure 3, exhaust gas from the top of a blast furnace 1 is compressed by a compressor 2 and then heated by preheaters 3 to a temperature of above 1250°C. Gas containing methane is compressed to a high pressure by a compressor 4 and then heated to a temperature of about 1000°C in a tube heater 5. The heated gas, the methane content of which having been decomposed by heating to about 1000°C in the tube heater 5, is mixed with the preheated furnace top gas at the exits of the

preheaters 3 and the mixture is then admitted into reformers 7 which provide a reforming zone in which the mixture is reformed to reducing gas. The heat required for the reaction is supplied by oxygen-fuel burners 6.

The following Examples are given by way of illustration only. The composition of the raw material gases and the resulting reducing gas and various reaction conditions are shown therein.

#### Example 1

Coke oven gas (C.O.G.) + blast furnace gas (B.F.G.)

Composition of the raw material gases.

	C.O.G. (%)	B.F.G. (%)
CO <sub>2</sub>	2.4	18.6
CO	5.9	23.8
O <sub>2</sub>	0.2	—
CH <sub>4</sub>	32.5	0.2
C <sub>m</sub> H <sub>n</sub>	3.8	—
H <sub>2</sub>	53.6	1.4
N <sub>2</sub>	1.6	56.0

Flow quantity	147 Nm <sup>3</sup> /hr	282 Nm <sup>3</sup> /hr
Pressure	1.2 kg/cm <sup>2</sup>	0.98 kg/cm <sup>2</sup>
Heating temperature	873°C	1438°C

Composition of the gas formed

CO <sub>2</sub>	3.3%
CO	30.5%
CH <sub>4</sub>	0.2%
H <sub>2</sub>	28.6%
N <sub>2</sub>	33.5%
Temperature	1211°C

#### Example 2

(CH<sub>4</sub> + N<sub>2</sub>) + B.F.G.

Composition of the raw material gases.

	(CH <sub>4</sub> + N <sub>2</sub> ) (%)	B.F.G. (%)
CO <sub>2</sub>	—	18.3
CO	—	24.1
O <sub>2</sub>	—	—
CH <sub>4</sub>	93.7	—
C <sub>m</sub> H <sub>n</sub>	—	—
H <sub>2</sub>	1.3	1.4
N <sub>2</sub>	4.8	56.2

Flow quantity	55 Nm <sup>3</sup> /hr	322 Nm <sup>3</sup> /hr
Pressure	1.18 kg/cm <sup>2</sup>	0.87 kg/cm <sup>2</sup>
Heating temperature	431°C	1367°C

Composition of the gas formed

CO <sub>2</sub>	4.7%
CO	39.3%
CH <sub>4</sub>	0.2%
H <sub>2</sub>	16.8%
N <sub>2</sub>	41.0%
Temperature	1232°C

From these Examples, it can be seen that

the resulting gas is highly reducing because it contains a large quantity of hydrogen and carbon monoxide.

The flow diagram shown in Figure 4 is substantially identical to that shown in Figure 3 except that the reformers 7 having oxygen-fuel burners 6 have been replaced by heat accumulating chambers 8. The process operates substantially in the same manner as that in Figure 3.

Figure 5 shows a comparison of the results obtained using the present invention compared with a hitherto proposed process. Curves identified by the letter I indicate the percent reaction between free carbon and CO<sub>2</sub> according to the present invention whereas those identified by the letter C indicate the percent reaction between free carbon and CO<sub>2</sub> according to a hitherto proposed process. Against each curve the first set of digits (such as 1450) indicate the temperature of reforming, the digits (in parentheses) indicate the retention time in the reforming zone in seconds and the third set of digits (such as 80) indicate the percentage of N<sub>2</sub> gas in the methane feed. Using a process according to the present invention, the percentage of reaction between free carbon and CO<sub>2</sub> increased by a factor of 2 to 3 compared with that of the hitherto proposed process, thereby resulting in only a small quantity of unreacted free carbon. Where a conventional catalyst is used in carrying out a process according to the invention, the quantities of the unreacted free carbon CO<sub>2</sub> and H<sub>2</sub>O can be reduced to negligible values. This can provide an efficient production of reducing gas for use in various reducing processes such as, for example iron melting, the production of sponge iron using a shaft furnace, and fluidized reducing processes.

#### WHAT WE CLAIM IS:—

1. A process for the production of reducing gas which comprises feeding a mixture of preheated methane or a methane-containing gas at a temperature below 1100°C and a gas comprising CO<sub>2</sub> and/or H<sub>2</sub>O at a temperature above 1250°C into a reforming zone, and heating the mixture at a temperature of at least 1200°C whereby the mixture is reformed.
2. A process according to claim 1 wherein the methane-containing gas comprises coke oven gas.
3. A process according to claim 1 wherein the methane-containing gas contains nitrogen.
4. A process according to any of claims 1 to 3 wherein the gas containing CO<sub>2</sub> and/or H<sub>2</sub>O comprises the exhaust gas from a blast furnace.
5. A process according to claim 1 or claim 2 wherein the methane-containing gas is coke oven gas and the gas containing CO<sub>2</sub> and/or H<sub>2</sub>O is the exhaust gas from a blast furnace

gas, the gases being fed to the reforming zone at a volume ratio of about 1:2.

- 5 6. A process according to claim 1 wherein the methane-containing gas is a mixture of methane and nitrogen, and the gas containing CO<sub>2</sub> and/or H<sub>2</sub>O is the exhaust gas from a blast furnace, the methane-containing gas and the gas containing CO<sub>2</sub> and/or H<sub>2</sub>O being fed to the reforming zone at a volume ratio of about 1:6.

10 7. A process according to any of claims 1 to 6 wherein the reforming zone has a fuel burner.

- 15 8. A process according to any of claims 1 to 7 wherein the reforming zone comprises a heat accumulating chamber.

9. A process for the production of reducing gas substantially as herein described.

10. A process for the production of reducing gas substantially as herein described with reference to either of the Examples.

11. Reducing gas when produced by a process according to any of the preceding claims.

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Fig. 1

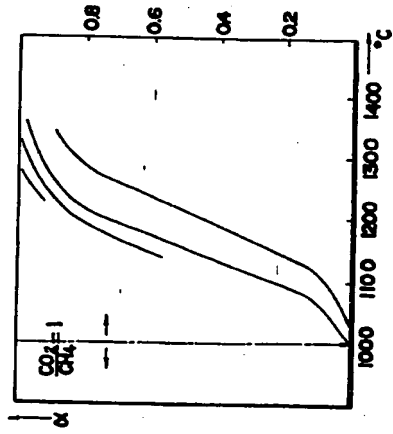


Fig. 2

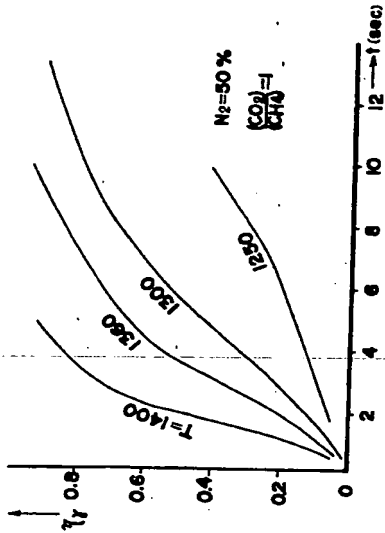


Fig. 3

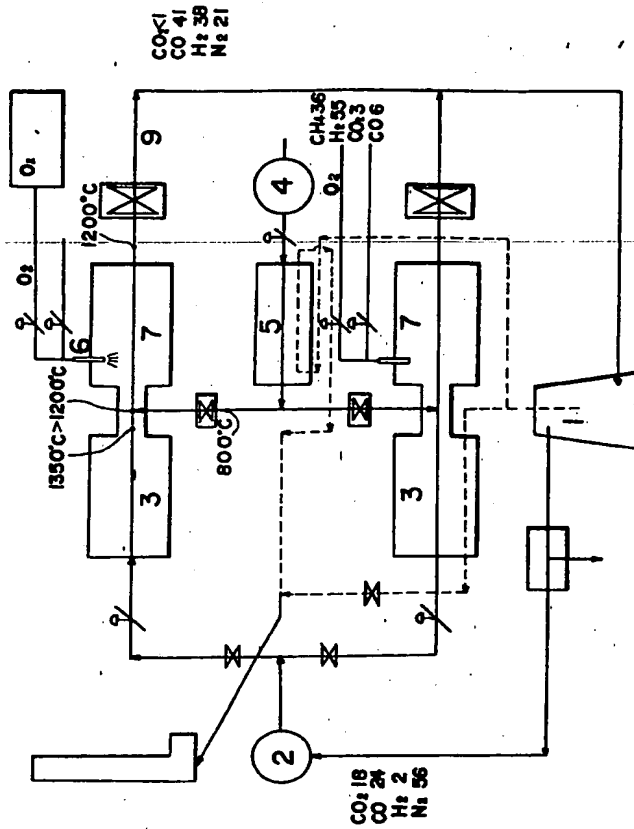


Fig. 4

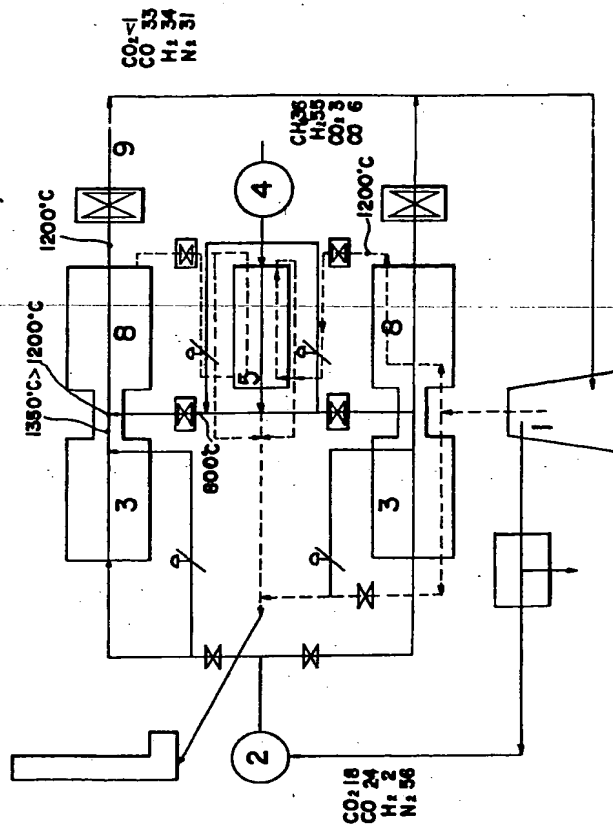
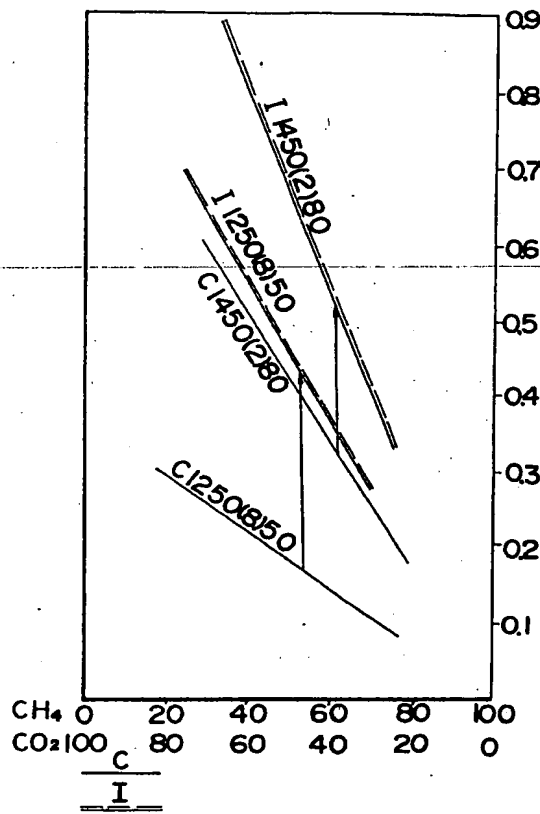


FIG. 5



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